ZESZYTY PROBLEMOWE POSTĘPÓW NAUK ROLNICZYCH 1981, z. 211

OPTIMALIZATION OF A DOMESTIC NICKEL-CATALYZED PROCESS OF HARDENING OF FATTY ACIDS

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Optimum working conditions were selected for a domestic nickel catalyst in experiments carried out according to a rotatable composite central second-order design. A full quadratic regression equation was obtained, the optimization of which allowed us to determine the most suitable temperature, pressure and time for the reaction of hardening development of new investigations on catalysts.

The hardening process has a long tradition in the fat technology, but as a catalytic process, it needs a systematic treatise, along with development of new inevstigations on catalysts.

The catalyst and conditions assuring its most effective action are the most important features in hydrogen addition to a double bond [1].

The optimum catalyst working conditions for hardening of fatty acids o low iodine values are those which assure the fastest rate of reduction of the unsaturated bonds in the acids. The problems associated with isomerization and selectivity may in this case be neglected as the final product should be deprived of unsaturated bonds [5].

The aim of this paper is to optimize the process of hardening of fatty acids catalyzed by a domestic catalyst. The catalyst is a powder containing about 45% of nickel, developed at this Institute's Catalysts. Division [1].

Mixed distilled animal fatty acids were used in the experiments. Their characteristics is given in Table 1.

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[1] The work was supervised by Asst. Prof. J. Berak and Asst. Prof. St. Grzelczyk.

Table 1

Characteristics of the raw material used in investigations (Mixed distilled utilisable fatty acids)

Property	Value
Acid value	202.5
Saponification value	215.2
Iodine value (Hanus method)	55.5
Unsaponifiable matter, %	0.30
Sulphur content, mg/kg	10.5
Ash content, weight %	0.35
Colour (iodine scale method)	9
Fatty acid composition by GLC method, weight %	
$C_{10:0}$	0.1
$C_{12:0}$	0.4
$C_{14:0}$	2.2
$C_{14:1}$	0.5
$C_{14:2}$	0.5
C_{15}	0.2
$C_{16:0}$	27.6
$C_{16:1}$	3.5
$C_{16:2}$	1.0
C_{17}	1.0
$C_{18:0}$	11.3
$C_{18:1}$	42.9
$C_{18:2}$	5.2
$C_{18:3}$	1.0
$C_{20:1}$	1.2
$C_{22:0}$	0.3
$C_{22:1}$	0.5

The hardening process was carried out in standard conditions in a 1-dm^3 autoclave made of acid-resistant steel. The autoclave was electrically heated and equipped with appropriate control and measuring devices.

The fixed process parameters included:

— electrolytic hydrogen, 99.5% pure,

— charge 500 g,

— mixing with a magnetic mixer, 200 r.p.m.,

— method of catalyst admission, viz., to the acids saturated with hydrogen at a temperature 30-40°C below the working temperature.

No samples were taken during the process. The amount of the catalyst was constant, 0.08% based on nickel. In each run, the amount used was too low to give complete saturation of the double bonds in the acids. This permitted evaluation of the process in terms of iodine values (measured by the Hanus method).

Table 2

Factorial design of experiments

No.	Variable level			Response function values	Notes
	x_1	x_2	x_3	y	
1	+1	+1	+1	38.4	2^n design
2	—1	+1	+1	40.7	for $n = 3$
3	+1	—1	+1	32.4	
4	—1	—1	+1	41.1	
5	+1	+1	—1	46.1	
6	—1	+1	—1	42.9	
7	+1	—1	—1	39.0	
8	—1	—1	—1	43.9	
9	0	0	0	33.8	centre of
10	0	0	0	31.4	design
11	0	0	0	34.7	
12	0	0	0	37.1	
13	0	0	0	38.5	
14	0	0	0	32.1	
15	—1.682	0	0	43.5	„star" points
					$x_1 = 16$ at
16	+1.682	0	0	35.4	$x_1 = 26$ at
17	0	—1.682	0	44.6	$x_2 = 133\,°C$
18	0	+1.682	0	40.5	$x_2 = 217\,°C$
19	0	0	—1.682	43.4	$x_3 = 1.33$ h
20	0	0	+1.682	27.2	$x_3 = 4.66$ h
x_1 pressures, ab. at.			—1 = 18	0 = 21 + 1 = 24	step = 3
temperatues, °C			—1 = 150	0 = 175 + + 1 = 200	step = 25
x_3 time, h			—1 = 2	0 = 3 + 1 = 4	step = 1
y iodine value					

The variables were:

— process temperature, which has a decisive effect on catalast activity [3],

— pressure, recognized to be a very significant factor [5],

— time of process.

The factorial experiment design is shown in Table 2.

The number of the experiments with 3 variables was $2^3 = 8$. Besides that, six measurements were made in the centre of the design for the determination of the replicate variance.

Six more experiments at the star points selected according to the rotatable central second-order design were taken to receive a full quadratic regression equation (Table 2) [4].

Table 3

Values of regression coefficients

Regression coefficients calculated for regression equation of the type:	
incomplete quadratic	full quadratic
$b_0 = 40.5625$	$b_0 = 34.5617$
$b_1 = -1.5875$	$b_1 = -1.92735$
$b_2 = 1.4625$	$b_2 = 0.351714$
$b_3 = -2.4125$	$b_3 = -3.40808$
$b_{12} = 1.8125$	$b_{11} = 1.96548$
$b_{13} = 1.1625$	$b_{22} = 3.06122$
$b_{23} = -0.0625$	$b_{33} = 0.498593$
$b_{123} = -0.2125$	$b_{12} = 1.8125$
	$b_{13} = -1.1625$
	$b_{23} = -0.0625$

Calculations were performed on a GIER computer in the GIER--Algol 4 language.

The procedure was as follows:

a) Regression coefficients were found for the type:

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{23}x_1x_2x_3$$

The coefficients are given in Table 3, Column 1.

b) The upper and lower confidence limits were determined for each coefficient by the Student's-test [4]. The intervals obtained correspon-ded to 95% probability level of the regression coefficient value.

For instance, for $b_1 = -1.5875$, the confidence limits for 95% probability are

$$(-1.648, -1.527)$$

c) The free term b_0 was verified on the basis of the experiments carried out at the centre of the design (null points). Thus, b_0 was 40.5625, compared with the experimental value 34.25.

d) Variance of the experiment was evaluated from the measurements made at the centre of the design. Its value was 5.55.

e) A significance test was made for each coefficient. Second order interactions, i.e. $x_1x_2x_3$, were found to be negligible. Therefore it was decided to continue inevstigations to obtain a more accurate model.

f) The model was extended to include quadratic terms and thereby a full quadratic regression equation was received.

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_2$$

For this, experimental data were amplified by including the expe-rimental results obtained at the star points chosen according to the

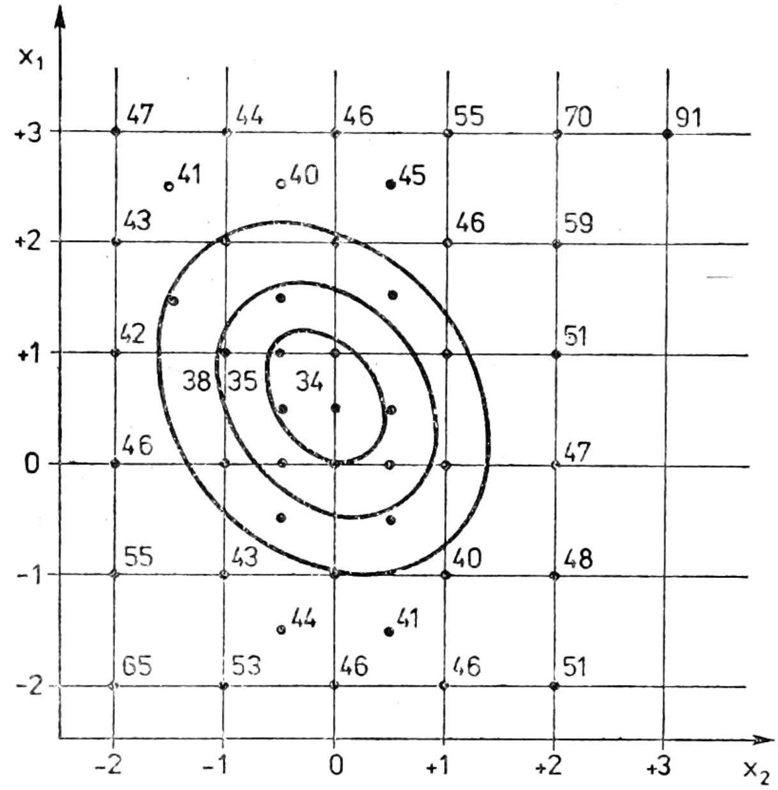

Fig. 1. Graphical expression of calculated from the full quadratic regression equation y values for variables x_1 and x_2 with x_3 on the 0 level

second-order rotatable design method. Measurements at the centre of the design were supplemented by two additional values (Table 2).

g) Regression coefficients were found for the full quadratic type equation. They are given in Table 3, Column 2.

h) Variance of the experiment was found to be 5.433 from additional results at the centre of the design.

i) Adequacy of the model was tested to a positive result. Value of test $F_{(5.5)} = 0.0519$ ($F_{cr} = 5.05$). The model was proved to be adequate and so optimization of equation

$$y = 34.5617 - 1.92735x_1 + 0.351714x_2 - 3.40808x_3 + 1.96545x_1^2 + \\ + 3.06122x_2^2 + 0.498593x_3^2 + 1.8125x_1x_2 - 1.1625x_1x_3 - 0.0625x_2x_3$$

was undertaken.

Optimization of the regression equation was carried out by Hoerles' ridge technique [2] in the following region:

$$-6 < x_1 < +3 \quad \text{(3-30 abs. atm.)}$$
$$-3 < x_2 < +2 \quad (125\text{-}225^\circ)$$
$$-2 < x_3 < +3 \quad \text{(1-6 hours)}$$

The global minimum received (iodine value = 31.2) has the following parameters

code values		real values
x_1	+0.3958	22.2 abs. atm.
x_2	—0.10284	172.4°C
x_3	+0.80795	3.8 h

Graphically this can be represented in a two-variable system, by assuming a constant duration of the process at the three hour level (code value 0) as in Figure 1.

Thus, the experiment executed according to the rotatable central composite second-order design allowed us to select the working conditions for the nickel catalyst with the distilled utilisable acids. The optimum conditions are as follows: pressure, 22 abs. atm., temperature, 170°C, time of reaction, about 4 hours.

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OPTYMALIZACJA PARAMETRÓW PROCESU UTWARDZANIA KWASÓW TŁUSZCZOWYCH WOBEC KRAJOWEGO KATALIZATORA NIKLOWEGO

Streszczenie

Utwardzanie kwasów tłuszczowych prowadzono w obecności katalizatora niklowego produkcji krajowej. Osiągnięcie maksymalnej skuteczności działania katalizatora wymaga przeprowadzenia optymalizacji parametrów.

Przeprowadzono procesy w warunkach standardowych w autoklawie 1 l (wsad 0,5 kg) z mieszadłem magnetycznym (szybkość mieszania 200 przesuwów na minutę). Jako parametry zmienne przyjęto temperaturę procesu, czas, ciśnienia wodoru. Katalizator (symbol WO59) dodawano w ilości 0,08% Ni.

Przebadano następujący zakres parametrów zmiennych:
temperatura 130-220°C (skok eksperymentu 25°C),
ciśnienie 14-26 (skok eksperymentu 2 atm),
czas 1-4 (skok eksperymentu 1 godz).

Jako parametr wyjściowy przyjęto spadek zawartości wiązań nienasyconych określany przez wartość liczby jodowej.

Wyniki przedstawiono w formie równań regresji.

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ОПТИМИЗАЦИЯ ПАРАМЕТРОВ ПРОЦЕССА ОТВЕРЖДЕНИЯ ЖИРНЫХ КИСЛОТ ПО ОТНОШЕНИЮ К ОТЕЧЕСТВЕННОМУ НИКЕЛЕВОМУ КАТАЛИЗАТОРУ

Резюме

Отверждение жирных кислот проводилось в присутствии никелевого катализатора отечественного производства. Обеспечение минимальной эффективности действия катализатора требует проведения оптимизации параметров.

Процессы проводились в стандартных условиях в автоклаве ёмкостью 1 л (загрузка 0,5 кг) с магнитным смесителем (скорость смешивания = 220 сдвигов в минуту). Вкачестве изменчивых параметров были приняты: температуры процесса, продолжительность, давление водорода. Катализатор (символ ВО 59) добавляли в количестве 0,08% Ni.

Исследовали следующие пределы изменчивых параметров:

температуру 130—220°C (шаг эксперимента 25°C),

давление 14—26 атм. (шаг эксперимента 2 атм.),

продолжительность 1—4 часа (шаг эксперимента 1 час).

В качестве исходного параметра было принято снижение содержания ненасыщенных связей определенное величиной иодного числа.